US 5104770

⑫ EUROPEAN PATENT APPLICATION

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�54 **Radiation-sensitive photoresist composition for exposure to deep ultraviolet radiation.**

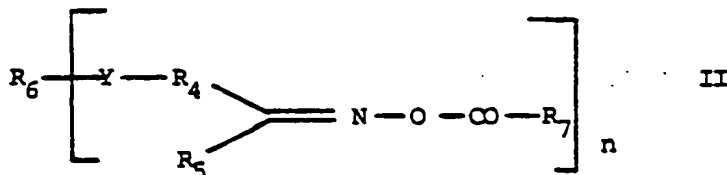�57 This invention relates to a new radiation-sensitive photoresist composition comprising an organic film-forming material and a radiation-sensitive compound which liberates a carboxylic acid on exposure to deep ultraviolet radiation and which is characterized in that said radiation-sensitive compound is an oxime carboxylic ester of the general formula I or II
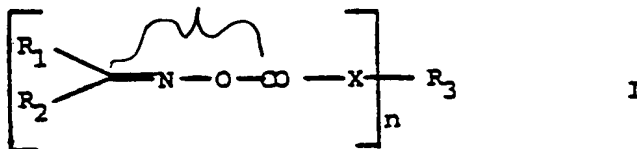
OR

The invention relates also to a process for formation of an image. The image-forming process may be used in the production of printing plates and microelectronic circuits.

EP 0 332 158 A2

Radiation-sensitive photoresist composition for exposure to deep ultraviolet radiation

This invention relates to a new radiation-sensitive positive photoresist composition comprising an organic film-forming material and a radiation sensitive compound which liberates a carboxylic acid on exposure to deep ultraviolet radiation.

In the production of an image using a positive photoresist, the portions of the resist that are exposed to
5   actinic radiation become more soluble in or more easily removed by a developer compared to the unexposed regions. Removal of the exposed regions by means of a developer, leaving the unexposed areas intact, results in the production of a positive image.

Generally commercially available positive photoresist compositions contain, in addition to an organic film-forming material which is usually a phenol-formaldehyde (novolac) resin, an o-naphthoquinone diazide
10 compound which decomposes on exposure to actinic radiation to produce an indene carboxylic acid with the evolution of nitrogen. Before exposure, the o-naphthoquinone diazide acts as a dissolution inhibitor for the organic film forming material. Upon exposure, however, the diazide is decomposed and completely loses its ability to act as an inhibitor and, in fact, becomes a dissolution enhancer. Thus, the dissolution rate of the exposed area becomes greater compared to that of the non-exposed areas.

15 However, there are several problems associated with the use of o-naphthoquinone diazides, foremost among these is their thermal instability. The diazides decompose at moderately elevated temperatures, even with protection from actinic radiation. This potential to decompose at moderately elevated tempera- tures renders the production of a quality image at high processing temperatures impossible. In addition, relatively large quantities of these diazides are required to make them useful as dissolution inhibitors. Also,
20 because they absorb very strongly in the deep ultraviolet region, photoresist compositions employing these diazides are relatively opaque to deep ultraviolet radiation and thus cannot be developed fully. This problem results because the radiation cannot penetrate deeply into the photoresist coating.

Attempts to correct the problems associated with the diazo-naphthoquinone inhibitors led to the production of 5-diazo Meldrum's acid and derivatives, as disclosed in US-A-4,339,522. Although these
25 materials, specifically designed for the deep ultraviolet region, were much more sensitive to the deep UV compared to the classical diazonaphthoquinone, these Meldrum's acid diazo compounds were not usable at high processing temperatures due to the fact that these compounds were evolved (sublimed) from the matrix resin to a significant extent at a relatively low temperature. Attempts to modify the structure of Meldrum's diazo led to several other problems, including insolubility in com mon casting solvents, as well
30 as the sublimation problem described above. This information is reported in IEEE Trans. Electron Dev., Vol. ED-28(11), 1300 (1981).

EP-A-0 241 423 to Demmer discloses positive working photoresist compositions using light sensitive oxime sulfonate compounds. Sulfonate oximes generally have a lower heat stability and are capable of crosslinking polymers at elevated temperatures.

35 A photoresist composition comprised of o-nitrobenzyl cholate inhibitor in poly(methylmethacrylate-co- methacrylic acid) (P(MMA-MAA)-resin), disclosed in US-A-4,666,820 issued May 19, 1987, (see also US-A- 4,400,461) was reported to be photoimageable employing deep ultraviolet radiation. Specifically, this composition was reported to yield surprisingly high contrasts. However, the mechanism reported for this photoreaction is not a completely conventional one; i.e. the mechanism involves inhibitor-assisted break-
40 down of the base-soluble P(MMA-MAA) resin in the exposed areas relative to the unexposed areas. The conventional mechanism, i.e. breakdown of the base-insoluble inhibitor into base-soluble fragment(s), leaving the resin binder entirely in tact, to produce a dissolution rate enhancement, is operating only to a very small extent. This information can be found in the Journal of Polymer Science: Polymer Chem. Ed., 21, 1975 (1983). The propensity for poly(methylmethacrylate) (PMMA) resin to degrade in the presence of deep
45 ultra violet radiation or free radicals is well known in the art. Other conventional base-soluble resins (e.g. novolac or poly(hydroxystyrene)) do not display this type of behavior. It would therefore be highly unlikely that a photoresist comprised of o-nitrobenzyl cholate inhibitor in novolak or poly(hydroxystyrene) resin could demonstrate the surprisingly high contrasts observed with P(MMA-MAA).

PMMA, compared to novolak or poly(hydroxystyrene), is also an undesirable resin for use in photores-
50 ists due to its extremely low plasma etch resistance.

In addition, the o-nitrobenzyl cholate/P(MMA-MAA) resist has been reported to possess poor dark field erosion resistance and relatively low sensitivity to 248 nm narrow band radiation. No high resolution patterns (e.g. < 1.0 micron) were obtainable under these conditions. This information is available in J. Vac. Sci. Technol. B., 5, 396 (1987).

It was therefore the problem to find a new positive-working photoresist composition, which possesses

high sensitivity to the deep ultraviolet region, producing quality, aqueous base developalbe images after exposure in a predetermined pattern. In addition, the dissolution inhibitor of this invention shall be stable toward thermal degradation.
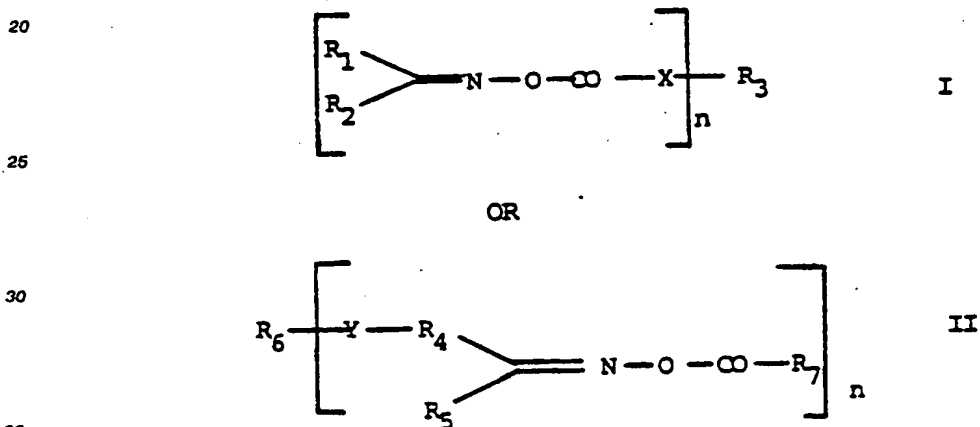
Now, it has been found that these problems can be sol ved by providing a positive-working radiation-sensitive photoresist composition comprising an organic film-forming material and a radiation-sensitive compound which liberates a carboxylic acid on exposure to deep ultraviolet radiation characterized in that the radiation-sensitive compound is an oxime carboxylate ester.

It has not been previously known that oxime carboxylate esters, when present with a base-soluble organic film-forming material, could suppress the dissolution rate of this film-forming material and that, after exposure to deep ultraviolet radiation, the oxime carboxylate ester would lose its ability to become a dissolution rate inhibitor and become a dissolution rate enhancer.

Because of the advantage that the dissolution inhibitor is highly stable toward thermal degradation it is allowed to produce images of high quality at relatively high processing temperatures.

Still another advantage of the present invention over the conventional o-naphthoquinone diazide-type systems is that the oxime carboxylate ester inhibitor compounds have little or no absorption of light in the conventional UV range (above 300 nm) and hence require no optical filters to obtain the higher resolution images available employing only shorter wavelength (deep UV) radiation.

In particular, the oxime carboxylate esters of the invention have the general formulae:

$$\left[\begin{array}{c} R_1 \\ R_2 \end{array} \right\rangle N - O - CO - X \right]_n R_3 \qquad I$$

OR

$$R_6 \left[Y - R_4 \underset{R_5}{\overset{}{\diagdown}} N - O - CO - R_7 \right]_n \qquad II$$

wherein the moieties
R_1, R_2, R_5 and R_7
are independently selected from hydrogen, monovalent aliphatic or aromatic groups and the moieties
X and Y
are selected from divalent aliphatic groups, oxy or thio or a direct covalent bond
R_4
represents a divalent alkylene of 1 to 6 carbons, or divalent arylene of 6 to 10 ring carbons and
R_6 and R_3
are monovalent or divalent moieties depending upon the value of the integer n which may be 1 to 18 carbon and aromatic groups of 6 to 10 ring carbons.

In a more preferred version
n is 1 or 2, preferably 1,
R_1 and R_2 are independently selected from hydrogen, or C_1-C_8-alkyl which is unsubstituted or substituted by -OH, -Cl, C_1-C_4-alkoxy, -CN, C_2-C_5-alkoxycarbonyl, phenyl, chlorophenyl, C_7-C_{10} alkylphenyl or C_7-C_{10}-alkoxyphenyl, benzoyl; or phenyl which is unsubstitued or substituted by -Cl, C_1-C_4-alkyl, C_1-C_4-alkoxy, in addition R_2 is C_2-C_8-alkoxycarbonyl, -CN, -NH$_2$, or -CONH$_2$; or
R_1 and R_2 together with the carbon atom to which they are bound form a C_4-C_{10}-cycloalkyl ring which may contain a carbonyl function alpha to the imino carbon; the most preferred composition is when R_1 and R_2 are both phenyl;
X and Y are independently selected from a direct bond, or it is -CH$_2$- or C_2-C_5-alkylene unsubstituted or substituted with -Cl, -Br, -CN, -NO$_2$, preferably a direct bond;

3

R_3 is, when n = 1, C_1-C_{18}-alkyl, phenyl which may be unsubstituted or substituted by halogen, C_1-C_{12}-alkyl, C_1-C_4-alkoxy, most preferably methoxy, or C_1-C_4-alkyl-CONH-, phenyl-CONH-, -NO$_2$ or benzoyl; or it is naphthyl which is unsubstituted or substituted by halogen, C_1-C_{12}-alkyl or C_1-C_4-alkoxy; or it is C_5-C_6-cycloalkyl, C_7-C_9-aralkyl, -CF$_3$, -CCl$_3$, -F, or NH$_2$, or R_3 and R_2 or R_3 and R_1 together with the atoms to which they are bonded, form a C_5-C_{12}-heterocyclic ring, and R_3 is, when n = 2, a (CH$_2$)$_n$ group, wherein m is 2 to 8, or phenylene or naphthylene each unsubstituted or substituted by C_1-C_{15}-alkyl, -Cl, -Br, -CN, NO$_2$, or -OCH$_3$; preferably R_3 is phenyl.

R_4 represents arylene, preferably phenylene, or it is a substituted arylene, methylene, C_2-C_6 straight, branched, or cyclic alkylene, optionally substituted by phenyl, naphthyl, or C_1-C_4-alkyl; and

R_5 is preferably phenyl, or it represents a hydrogen atom; C_1-C_8-alkyl, optionally substituted by -OH, -Cl, C_1-C_4-alkoxy, CN, C_2-C_5-alkoxycarbonyl, phenyl, chlorophenyl, C_7-C_{10}-alkylphenyl; or it is C_7-C_{10}-alkoxyphenyl which may be optionally substituted by -Cl, C_1-C_4 alkyl, or C_1-C_4-alkoxy; C_2-C_8-alkoxycarbonyl; or CN, or -NH$_2$, or benzoyl, or alkoxyl, and

R_6 is, when n = 1, preferably a hydrogen atom, or it is C_1-C_8-alkyl, or phenyl, substituted phenyl, or halogen; or R_5 and R_6 together with the atoms to which they are bound can form a C_6-C_{12}-carbocyclic or heterocyclic ring.

R_7 is preferably phenyl unsubstituted or substituted by alkoxy, most preferably methoxy, or halogen, or NO$_2$, or it represents C_1-C_{18} straight or branched alkyl which may be optionally substituted by halogen or C_1-C_4-alkoxy; or it is C_6-C_{12}-aryl; optionally substituted by C_1-C_{15}-alkyl, or NO$_2$; C_5-C_6-cycloalkyl, or R_7 and R_5, together with the atoms to which they are bound, form a C_6-C_{12}-heterocyclic ring.

In particular preferred oxime carboxylate esters are
O-anisoylbenzophenone oxime;
O-benzoylacetophenone oxime;
di(O-lauroyloxy)diphenylglyoxime;
O-benzoylcyclohexanone oxime;
O-benzoylbenzamidoxime;
O-anisoyl-α-hydroxyiminobenzyl cyanide;
O-lauroyloxybenzophenone oxime;
and mixtures thereof.

Compounds of the above type are described in US-A-4,590,145 as photopolymerization initiators for ethylenically unsaturated monomers.

The oxime carboxylate esters of the invention can be easily prepared in good yield by reaction of a compound bearing oxime functionality with a compound bearing carbonyl chloride functionality in the presence of a suitable base, such as pyridine or triethylamine, or N-methylmorpholine, in a suitable organic solvent, such as N-methylpyrrolidinone, N,N-dimethylacetamide, N,N-dimethylformamide, methylene chloride, tetrahydrofuran, propylene glycol methyl ether acetate. Preferably, the reaction is carried out in a solvent that can also act as a base, such as pyridine. The product can be precipitated from the reaction mixture by the addition of the reaction mixture to a solvent, which is being stirred, that is miscible with the reaction solvent, yet immiscible with the desired product. Such a procedure can be exemplified by the addition of an N-methylpyrrolidinone solvent reaction mixture into water that is being agitated or stirred. Alternatively, the product could be isolated by washing an organic reaction mixture with water to remove water miscible salts and then evaporating the organic solvent to dryness to recover the desired product. The oxime carboxylate esters obtained from this procedure are usually recrystallized from a suitable solvent; however, the product obtained from the reaction mixture before recrystallization is usually sufficiently pure for use in the present invention. The starting oxime containing compound, if not available from commercial chemical suppliers, can be easily prepared by conventional synthetic procedures. Examples of these types of preparations may be found in "The Systematic Identification of Organic Compounds", John Wiley and Sons, New York, 1980, p. 181, or Die Makromoleculare Chemie, 1967, 108, 170, or Organic Synthesis, 1979, 59, 95.

The organic film-forming material which is soluble in aqueous base is preferably one containing phenolic hydroxyl groups or a phosphonic, phosphoric, carboxylic, or sulfonic acid groups.

Such film forming materials include novolac resins which are prepared from an aldehyde such as acetaldehyde or furaldehyde, preferably formaldehyde, with a phenol such as phenol itself, phenol substituted by 1 or 2 chlorine atoms, such as p-chlorophenol, or 1 or 2 alkyl groups of 1 to 9 carbon atoms each, e.g., o-, m-, p-cresol, the xylenols, p-tert.butyl phenol, and p-nonylphenol, p-phenylphenol, resorcinol, bis(4-hydroxyphenyl)methane, and 2,2-bis(4-hydroxyphenyl)methane.

Other suitable film forming materials include homopolymers and copolymers of ethylenically unsaturated car boxylic acids and carboxylic acid anhydrides. These materials include copolymers or acrylic and

methacrylic acids with, for example, vinyl aromatic compounds such as styrene, or substituted styrenes, including preferably homopolymers and copolymers of hydroxystyrene and phenyl ring-substituted hydroxystyrene.

Additional film forming materials are carboxyl-terminated polyesters such as those obtainable by
5 reaction of a dihydric alcohol with a dicarboxylic acid. Dihydric alcohols which may be employed include ethylene glycol, diethylene glycol, and higher polyoxyethylene glycols; propane-1,2-diol, dipropylene glycol, and higher polyoxypropylene glycols; propane-1,3-diol; butane-1,4-diol and polyoxytetramethylene glycols; pentane-1,5-diol, resorcitol, bis(4-hydroxycyclohexyl)methane, and 2,2-bis(4-hydroxycyclohexyl)propane. Dicarboxylic acids which may be employed include aliphatic acids such as succinic, glutaric, adipic,
10 pimelic, suberic, azelaic, or sebacic acids, dimerized linoleic acid, aromatic acids such as phthalic, isophthalic, and terephthalic acids, and cycloaliphatic acids such as hexahydrophthalic acid.

Also suitable film forming materials are acid group-containing adducts of polyepoxides having an average, more than one 1-2 epoxide groups per molecule, with polycarboxylic acids, especially dicarboxylic acids, or with substances which contain a carboxylic, sulphonic, phosphonic or phosphoric acid group and
15 also a group which reacts preferentially, under the conditions used for adduct formation, with the epoxide groups of the polyepoxide. Such a group is conveniently a primary or secondary aliphatic or aromatic amino group, or a mercapto group.

In particular, the radiation-sensitive composition is being substantially free from ethylenically unsaturated material which is polymerizable by means of free radicals.
20   A further aspect of this invention is a process for the production of an image comprising by

a) coating a layer of said radiation-sensitive composition onto a substrate,

b) imagewise exposing said coated substrate to radiation, and

c) treating the exposed substrate with aqueous base developer to remove said composition in the exposed areas.
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The process of this invention is carried out by first coating a layer of the photosensitive composition of the invention onto a substrate from a solvent, such as N-methylpyrrolidinone, methyl ethyl ketone, cyclopentanone, propylene glycol mono methyl ether acetate, 2-ethoxy ethyl acetate, N,N-dimethylformamide, or mixtures thereof, in a conventional manner, such as by dip, roll, spray coating, or preferably
30 spin coating.

The residual solvent is evaporated either by air-drying or heating, optionally under reduced pressure. The substrate may be copper, aluminum or other metal, synthetic resin or plastic, such as a film for a polyester, a polyamide, polyimide, a polyolefin, or silicon oxide, or silicon nitride. The composition is applied such that the resist layer, after drying, is between about 0.3 and 200 microns thick, preferably
35 between 0.5 and 2.0 microns thick.

The exposure of the composition to actinic radiation in a predetermined pattern may be achieved by exposure through a suitable image-bearing mask consisting of opaque and transparent areas. The oxime carboxylate ester which liberates a carboxylic acid on exposure to deep ultraviolet radiation is thereby effecting an enhancement of the dissolution rate of film-forming material in aqueous base. Deep ultraviolet
40 radiation is employed in the range of 180 - 300 nm, preferably 220 - 280 nm, and suitable sources include deuterium arcs, mercury vapor arcs, xenon-mercury arcs, pulsed mercury arcs, xenon arcs, and various laser sources, such as the krypton-fluoride excimer laser. The exposure time required depends on several factors such as the nature of the composition employed, the thickness of the layer, the type of radiation source, and the distance of the radiation source from the layer. The exposure time is generally on the order
45 of 10 seconds to 4 minutes, but can be readily determined by routine experimentation.

After the resist layer is image-wise exposed, it is washed with an aqueous base developer to remove the exposed areas, leaving the unexposed areas. The developer thus dissolves or renders much more easily removed the exposed areas, and gentle agitation may be employed if necessary.

The aqueous base developer can be an aqueous solution of a strong base such as N-methylmor-
50 pholine; however, an aqueous alkaline solution, such as one containing sodium hydroxide, sodium carbonate, sodium bicarbonate, tetramethylammonium hydroxide, or the like, is preferred. A very small amount, generally 5 - 15 % by volume, of a water-soluble lower alcohol may be added to the developer solution to speed development, if necessary.

The image-forming process may be used in the production of printing plates and microelectronic
55 circuits.

After the exposure and development steps, the substrate may be etched. There are several reasons why etching may be employed, including the desire to remove metal from the exposed areas in the formation of a printed circuit, or the desire to increase the depth of image. Suitable etching procedures are

well known in the art.

Example I

Preparation of O-Anisoylbenzophenone Oxime
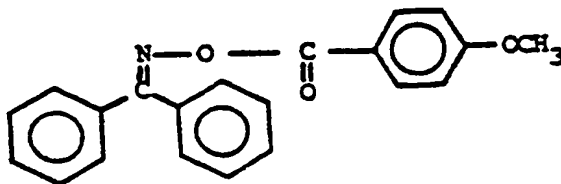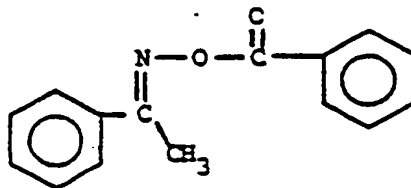

a) Preparation of Benzophenone Oxime

A 500 ml flask was fitted with a reflux condenser and charged with hydroxylamine hydrochloride (8.40 g, 0.12 mole), ethanol (200 ml), pyridine (9.71 ml, 0.12 mole) and benzophenone (20.0 g, 0.11 mole). After heating at reflux with stirring for 2 hours, ethanol (100 ml) was removed by distillation and the flask allowed to stand at room temperature for 4 hours. During this time, cyrstals formed and they were removed by vacuum filtration. The reaction product was recovered in amount of 20.0 g (92 %), mpt. 134 - 136° C; IR absorption (KBr): ν(C = N) 1,500 cm^{-1}(m), ν(N-OH) 3,240 cm^{-1}(m).

b) Preparation of O-Anisoylbenzophenone Oxime

A 500 ml, three-neck flask was fitted with a septum, a nitrogen gas inlet and a ground glass stopper. The apparatus was purged with nitrogen and charged with pyridine (400 ml) and benzophenone oxime (15 g, 0.075 mole). After the solution was homogenous, p-anisoyl chloride (14.5 g, 0.085 mole) was injected slowly, dropwise into solution. After stirring at room temperatur overnight, the solution was added slowly to cold water under agitation to precipitate a white solid. Crystallization from ethanol afforded colorless plates: 21.2 g (84 %); mpt. 152 - 153° C; IR absorption (KBr): ν(C = O) 1,740 cm^{-1} (s); mass spectrum: M* 332 (1.40 %), m/e 180 [M-OCOC₆H₄OCH₃] (100 %); UV absorption: λmax (ϵm): 272 nm (27,400), 195 nm (60,970).

Example II

Preparation of O-Benzoylacetophenone Oxime

a) Preparation of Acetophenone Oxime

Acetophenone oxime was prepared from acetophenone as described in Example Ia. mpt. 48 - 49° C; IR absorption (KBr): ν(C = N) 1,510 cm^{-1} (m).

b) Preparation of O-Benzoylacetophenone Oxime

O-Benzoylacetophenone oxime was prepared from pyridine (75 ml), acetophenone oxime (12.0 g, 0.089 mole), and benzoyl chloride (11.4 ml, 0.098 mole) as in Example Ib. Crystallization from ethanol afforded colorless needles: 17.2 g (81 %); mpt. 95 - 96° C, IR absorption (KBr): ν(C = O) 1,750 cm^{-1}(s); mass spectrum M* 239 (3.5 %), m/e 118 [M-OCOPh] (30 %), m/e 105 (100 %); UV absorption: λmax. (ϵm) 248 nm (20,900), 195 nm (44,350).

Example III

Preparation of Di(O-lauroyloxy)diphenylglyoxime
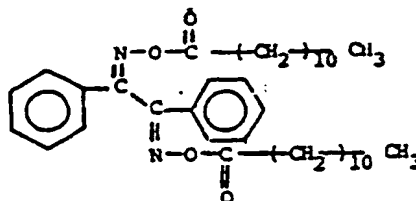
Di(O-lauroyloxy)diphenylglyoxime was prepared from pyridine (75 ml), diphenyl glyoxime (10.0 g, 0.042 mole), and lauroyl chloride (20.4 ml, 0.088 mole) as in Example Ib. Crystallization from ethanol gave fluffy, colorless needles: 24.1 g (95 %) mpt. 77 - 78° C; IR absorption (KBr): ν(CH) 2,860 cm^{-1} and 2,880 cm^{-1}-(m); ν(C = O) 1,780 cm^{-1}(s); mass spectrum: M* 605 (10.5 %); UV-absorption:λmax (ϵm) 224 nm (16,300).

Example IV

Preparation of O-Benzoylcyclohexanone Oxime
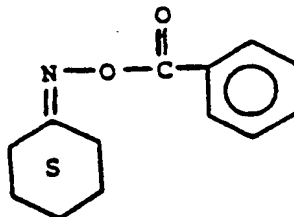
O-Benzoylcyclohexanone oxime was prepared from pyridine (75 ml), cyclohexanone oxime (ALDRICH, 15 g, 0.13 mole), and benzoyl chloride (15.4 ml, 0.13 mole) as in Example Ib. Crystallization from ethanol/water gave colorless plates: 21.7 g (77 %); mpt. 60 - 61° C; IR absorption (KBr): ν(CH) 2,860 cm^{-1} and 2,880 cm^{-1}(m), ν(C = O) 1,740 cm^{-1}(s); mass spectrum: M* 217 (1.8 %), m/e [105 M-(CH$_2$)$_5$C = NO] (100 %); UV-absorption: λmax (ϵm): 230 nm (14,100).

## Example V

Preparation of O-Benzoylbenzamidoxime
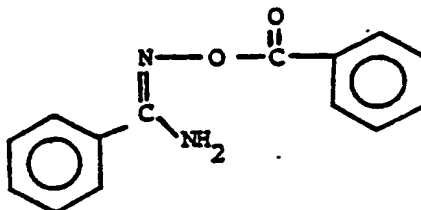
a) Preparation of Benzamidoxime

An one liter round-bottom flask was fitted with a reflux condenser and charged with hydroxylamine hydrochloride (36.7 g, 0.52 mole) water (50 ml), sodium hydroxide (20.8 g, 0.52 mole) in water (50 ml) and ethanol (75 g). The solution was cooled to 0° C with an ice-water bath. Benzonitrile (50.0 g, 0.48 mole) in ethanol (60 g) were added to solution, and the reaction was heated to reflux for 14 hours. After removing the ethanol by evaporation, the aqueous mixture was extracted with ether (250 ml) and the organics were dried (Na₂SO₄). Removal of the ether left an orange, oily solid which crystallized from toluene as colorless needles: 49.5 g (76 %); mpt. 75 - 77° C; IR absorption (KBr): ν(NH) 3,440 cm⁻¹ and 3,380 cm⁻¹; ν(C = N) 1,645 cm⁻¹(s);

b) Preparation of O-Benzoylbenzamidoxime

A 500 ml, three-neck flask was fitted with a septum, a nitrogen gas inlet and a ground glass stopper. The apparatus was purged with nitrogen and charged with benzamidoxime (15 g, 0.11 mole), benzene (200 ml), and triethylamine (16.9 ml, 0.12 mole). The mixture was cooled to 10° C and benzoyl chloride (13.9 ml, 0.12 mole) was injected slowly into solution. After stirring at 10° C for 2 hours, the precipitate was filtered off and washed copiously with ice-water and air-dried. Crystallization from ethanol gave colorless needles: 20.5 g (77%); mpt. 148° C; IR absorption (KBr): ν(C = O) 1.730 cm⁻¹; mass spectrum: M⁺ 240 (32 %), m/e 105 [M-C₆H₅CH₂NH₂] (100 %); UV absorption: λmax. (ϵm): 260 nm (6,800); 224 nm (10,900); 195 nm (37,100).

Example VI

Preparation of O-Anisoyl-α-hydroxyiminobenzyl cyanide
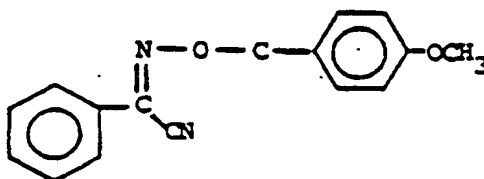
a) Preparation of α-Hydroxyiminobenzyl cyanide

α-Hydroxyimino cyanide was prepared in 56 % yield according to the procedure detailed in Org. Syn., 1979, 59, 95 mpt: 119 - 121° C IR absorption (KBr): ν(N-OH) 3,380 cm^{-1}(s); ν(C = N) 2,220 cm^{-1}(w).

5 b) Preparation of O-Anisoyl-α-hydroxyiminobenzylcyanide

O-Anisoyl-α-hydroxyiminobenzyl cyanide was prepared from α-hydroxyiminobenzyl cyanide (12.0 g, 0.083 mole), pyridine (100 ml), and p-anisoyl chloride (14.1 g, 0.083 mole) as in Example Ib. Crystallization from ethanol/water gave colorless plates, mpt. 155 - 160° C; 18.5 g (80 %); IR absorption (KBr): ν(C = N) 10 2,220 cm^{-1}(w); ν(C = O) 1,760 cm^{-1}(s); mass spectrum: M$^{\bullet}$ 281 (160 %), m/e 135 [M-C$_6$H$_5$CNO(CN)] (100 %); UV absorption λmax (εm): [THF] 250 nm (11,680), 295 nm (27,000).

Example VII

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Preparation of O-Lauroyloxybenzophenone Oxime

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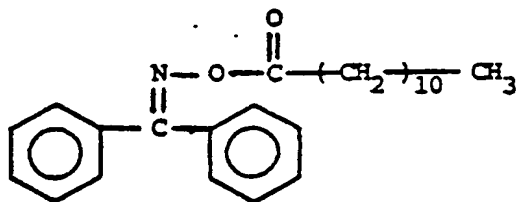
30 O-Lauroyloxybenzophenone oxime was prepared with pyridine (75 ml), benzophenone oxime (15.0 g, 0.076 mole), and lauroyl chloride (17.6 ml, 0.076 mole) as in Example Ib. Crystallization from ethanol gave colorless, long needles: 24.7 g (86 %); mpt. 48 - 49° C; IR absorption (KBr): ν(CH) 2,860 cm^{-1} and 2,820 cm^{-1} (s), ν(C = O) 1,780 cm^{-1}(s); mass spectrum: M$^{\bullet}$ 380 (1.8 %), m/e 180 [M-OCO(CH$_2$)$_{10}$CH$_3$] 100 %, UV absorption: λmax (εm) 250 nm (12,500), 200 nm (25,000).

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Example VIII

Lithographic Evaluation of O-Anisoylbenzophenone Oxime in Cresol-Formaldehyde Resin

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A formulation was prepared consisting of 3 p.b.w. O-Anisoylbenzophenone oxime, 24 p.b.w. cresol-formaldehyde resin, 73 p.b.w. and propylene glycol monomethyl ether acetate solvent. The resist was spun onto a silicon wafer and baked at 90° C for 30 minutes to give a 1.4 micron film. The film was exposed to the full spectrum of an OAI Deep UV source through a quarz optoline gradient mask. Development with 45 buffered, aqueous potassium hydroxide solution gave clearly developed open areas and patterns.

Example IX

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Lithographic Evaluation of O-Benzoylbenzamidoxime In Cresol-Formaldehyde Resin

3 p.b.w. O-Benzoylbenzamidoxime was formulated in 24 p.b.w. cresol-formaldehyde resin as in Example VIII. Irradiation of a similarly formed film through a 260 nm interference filter gave a clear, positive 55 image.

Example X

Lithographic Evaluation of O-Anisoylbenzophenone Oxime in Poly(4-hydroxystyrene) Resin

3 p.b.w. O-Anisoylbenzophenone Oxime was formulated in 24 p.b.w. poly(4-hydroxystyrene) resin as in Example VIII. Irradiation of a similarly formed film to the full spectrum of an HTG Deep UV source through a

5 quartz mask gave, after development with buffered, aqueous potassium hydroxide solution, clearly developed open areas and patterns.

Claims

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1. Positive-working radiation-sensitive photoresist composition comprising an organic film-forming material and a radiation-sensitive compound which liberates a carboxylic acid on exposure to deep ultraviolet radiation characterized in that the radiation-sensitive compound is an oxime carboxylic ester.

2. Radiation-sensitive composition according to claim 1 characterized in that said oxime carboxylic ester

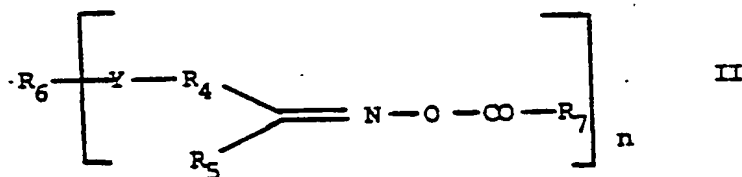15 has the general formulas I or II:

OR
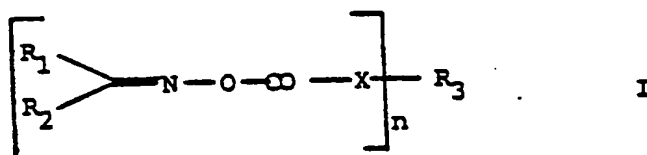
wherein: n is an integer of 1 or 2

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R_1 and R_2 are independently selected from hydrogen, or C_1-C_8-alkyl which is unsubstituted or substituted by -OH, -Cl, C_1-C_4-alkoxy, -CN, C_2-C_5-alkoxycarbonyl, phenyl, chlorophenyl, C_7-C_{10} alkylphenyl or C_7-C_{10}-alkoxy phenyl, benzoyl; or phenyl which is unsubstitued or substituted by -Cl, C_1-C_4-alkyl, C_1-C_4-alkoxy, in addition R_2 is C_2-C_8-alkoxycarbonyl, -CN, -NH_2, or -$CONH_2$; or

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R_1 and R_2 together with the carbon atom to which they are bound form a C_4-C_{10}-cycloalkyl ring which may contain a carbonyl function alpha to the imino carbon;

X and Y are independently selected from a direct bond, or it is -CH_2- or C_2-C_5-alkylene unsubstituted or substituted with -Cl, -Br, -CN, -NO_2;

R_3 is, when n = 1, C_1-C_{18}-alkyl, phenyl which may be unsubstituted or substituted by halogen, C_1-C_{12}-alkyl,

45 C_1-C_4-alkoxy, or C_1-C_4-alkyl-CONH-, phenyl-CONH-, -NO_2 or benzoyl; or it is naphthyl which is unsubstituted or substituted by halogen, C_1-C_{12}-alkyl or C_1-C_4-alkoxy; or it is C_5-C_6-cycloalkyl, C_7-C_9-aralkyl, -CF_3, -CCl_3, -F, or NH_2, or R_3 and R_2 or R_3 and R_1 together with the atoms to which they are bonded, form a C_5-C_{12}-heterocyclic ring, and R_3 is, when n = 2, a $(CH_2)_m$ group, wherein m is 2 to 8, or phenylene or naphthylene each unsubstituted or substituted by C_1-C_{15}-alkyl, -Cl, -Br, -CN, NO_2, or -OCH_3;

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R_4 represents arylene, preferably phenylene, or it is a substituted arylene, methylene, C_2-C_6 straight, branched, or cyclic alkylene, optionally substituted by phenyl, naphthyl, or C_1-C_4-alkyl;

R_5 is preferably phenyl, or it represents a hydrogen atom; C_1-C_8-alkyl, optionally substituted by -OH, -Cl, C_1-C_4-alkoxy, CN, C_2-C_5-alkoxycarbonyl, phenyl, chlorophenyl, C_7-C_{10}-alkylphenyl; or it is C_7-C_{10}-alkoxyphenyl which may be optionally substituted by -Cl, C_1-C_4 alkyl, or C_1-C_4-alkoxy; C_2-C_8-alkoxycarbonyl; or CN, or -NH_2, or benzoyl, or alkoxyl;

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R_6 is, when n = 1, hydrogen atom, or it is C_1-C_8-alkyl, or phenyl, substituted phenyl, or halogen; or R_5 and R_6 together with the atoms to which they are bound can form a C_6-C_{12}-carbocyclic or heterocyclic ring; and R_7 is phenyl unsubstituted or substituted by alkoxy, or halogen, or NO_2, or it represents C_1-C_{18} straight or

branched alkyl which may be optionally substituted by halogen or C_1-C_4-alkoxy; or it is C_6-C_{12}-aryl; optionally substituted by C_1-C_{15}-alkyl, or NO_2; C_5-C_6-cycloalkyl, or R_7 and R_9, together with the atoms to which they are bound, form a C_6-C_{12}-heterocyclic ring.

3. Radiation-sensitive composition according to claim 2, characterized in that R_1, R_2, R_5 and R_7 are phenyl which is unsubstituted or substituted.

4. Radiation-sensitive composition according to claims 2 and 3, characterized in that X and Y represent a direct bond.

5. Radiation-sensitive composition according to claims 2 to 4, characterized in that n equal 1.

6. Radiation-sensitive composition according to claims 2 to 5, characterized in that said oxime carboxylate ester is selected from

O-anisoylbenzophenone oxime;

O-benzoylacetophenone oxime;

di(O-lauroyloxy)diphenylglyoxime;

O-benzoylcyclohexanone oxime;

O-benzoylbenzamidoxime;

O-anisoyl-α-hydroxyimino-benzylcyamide;

O-lauroyloxybenzophenone oxime;

and mixtures thereof.

7. Radiation-sensitive composition according to claims 1 to 6, characterized in that the organic film-forming material consisting essentially of an aqueous base soluble material.

8. Radiation-sensitive composition according to claims 1 to 7, characterized in that said organic film-forming material having a phenol hydroxyl group or a carboxylic, sulfonic, phosphonic or phosphoric acid group.

9. Process for forming an image which comprises

a) coating a layer of said radiation-sensitive layer according to claims 1 to 8 onto a substrate,

b) imagewise exposing said coated substrate to radiation, and

c) treating the exposed substrate with aqueous base developer to remove said composition in the exposed areas.

10. Process according to claim 9, wherein the exposure is achieved by using a suitable image-bearing mask and deep ultraviolet radiation in the range of 180 to 300 nm.

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